

Supporting Information

## Viscoelastic Change of Block Copolymer Ion Gels in a Photo-switchable Azobenzene Ionic Liquid Triggered by Light

Caihong Wang,<sup>†a,b</sup> Kei Hashimoto,<sup>†b</sup> Ryota Tamate,<sup>b</sup> Hisashi Kokubo,<sup>b</sup> Ken Morishima,<sup>c</sup> Xiang Li,<sup>d</sup>

Mitsuhiro Shibayama,<sup>d</sup> Fengniu Lu,<sup>e</sup> Takashi Nakanishi<sup>e</sup>, and Masayoshi Watanabe<sup>\*b</sup>

<sup>a</sup> *Department of Chemical Machinery and Control Engineering, School of Chemical Engineering, Sichuan University, Sichuan 610065, China*

<sup>b</sup> *Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*

<sup>c</sup> *Institute for Integrated Radiation and Nuclear Science, Kyoto University, Kumatori, Osaka 590-0494, Japan*

<sup>d</sup> *Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

<sup>e</sup> *National Institute for Materials Science (NIMS) 1-2-1 Sengen, Tsukuba 305-0047, Japan*

---

† These authors contributed equally to the paper.

\* Corresponding author. E-mail: [mwatanab@ynu.ac.jp](mailto:mwatanab@ynu.ac.jp)

## 1. Experimental

### 1.1. Materials

CuBr and CuBr<sub>2</sub> were dried for 12 h at 60 °C under a vacuum. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA) was purchased from TCI. 1-Butylimidazole, 1-methylimidazole, methyl methacrylate (MMA), and benzyl methacrylate (BnMA) were purchased from TCI and distilled at reduced pressure prior to use. Phenethyl methacrylate (PhEtMA) and Azo-IL were synthesized as previously reported.<sup>1-2</sup> All other chemical reagents were used as received, unless otherwise noted.

### 1.2 Synthesis of PMMA macroinitiator

A PMMA macroinitiator was synthesized via ATRP with a bifunctional initiator. A pre-dried mixture of CuBr (16 mg, 0.11 mmol), CuBr<sub>2</sub> (1.0 mg, 4.5 μmol), and PMDETA (39 μL, 0.19 mmol) was dissolved in anisole (40 mL) at room temperature to obtain a transparent solution. MMA (20 mL, 0.19 mol) and bifunctional initiator (37.6 mg, 0.34 mmol) were added to the solution at room temperature. After being degassed three times by freeze-pump-thaw cycles, polymerization was carried out at 60 °C for 6 h and terminated by quenching the solution with dry ice/methanol. The products were dissolved in chloroform and purified by column chromatography (alumina) and repetitive reprecipitation in methanol. PMMA was characterized using <sup>1</sup>H-NMR spectroscopy and size exclusion chromatography (SEC). The number-average molecular weight ( $M_n$ ) was calculated by <sup>1</sup>H-

NMR, and the polydispersity ( $M_w/M_n$ , where  $M_w$  is the weight-average molecular weight) was determined by SEC calibrated with PMMA standards using tetrahydrofuran (THF) as the eluent (Figure S1). Table S1 shows the related results.

**Table S1.** Molecular weight and polydispersity index (PDI) of polymers synthesized in this study.

	$M_n$ (kDa) <sup>a</sup>	PDI ( $M_w/M_n$ ) <sup>b</sup>
PMMA <sup>c</sup>	42	1.13
BMB	32-42-32	1.10
PMP	30-42-30	1.16

<sup>a</sup>  $M_n$  of PMMA was estimated using <sup>1</sup>H-NMR.  $M_n$ s values of BMB and PMP were calculated from the results of <sup>1</sup>H-NMR based on the PMMA precursor.

<sup>b</sup> Determined by SEC analysis in THF.

<sup>c</sup> Macroinitiator of BMB.

### 1.3 Synthesis of triblock copolymer BMB and PMP

BMB was prepared as follows. A pre-dried mixture of CuBr (32 mg, 0.23 mmol) and CuBr<sub>2</sub> (1.0 mg, 4.5 μmol), PMMA macro initiator (9.5 g, 0.23 mmol), BnMA (15 g, 85 mmol), and PMDETA (57 μL, 0.27 mmol) was mixed in anisole (90 mL) at room temperature. Then, the homogeneous solution was degassed three times by freeze-pump-thaw cycles, and polymerization was carried out at 80 °C and terminated by quenching the solution with dry ice/methanol. The product was purified by column chromatography (alumina) and reprecipitation twice using ethyl acetate as a good solvent and methanol as a poor solvent. BMB was dried for 8 h at 65 °C under a vacuum. PMP was also prepared in a similar

way to the BMB block copolymer. The block copolymers were characterized using a similar method to that for PMMA (**Figure 1**), as listed in **Table S1**.

#### 1.4 Sample preparation for measurements

The polymer solutions were prepared by the co-solvent method. Polymers were first dissolved in THF as a co-solvent. An appropriate amount of IL mixture was added to the THF solution and stirred for 6 h to obtain a transparent solution. THF in the polymer solution was removed under reduced pressure while heating at 60 °C for 24 h. The volume fractions of the components are listed in **Table S2**.

**Table S2.** Volume fractions in the samples.

	$f_{IL}^a$	$f_P, f_B^b$	$f_M^c$
20 wt% PMP/IL	0.711	0.167	0.121
20 wt% BMB/IL	0.719	0.163	0.118

<sup>a</sup> Volume fractions of ionic liquid ( $f_{IL}$ ).

<sup>b</sup> Volume fractions of PhEtMA (in 20 wt.% PMP/IL,  $f_P$ ) and BnMA (in 20 wt.% BMB/IL,  $f_B$ ).

<sup>c</sup> Volume fractions of PMMA ( $f_M$ ).

## 1.5 UV source

A 500-W high-pressure mercury lamp (Ushio Optical Modulex BA-H500) was used to irradiate the sample at a tuned intensity and wavelength by glass filters (UV light: 366 nm,  $\Delta\lambda$  30 nm, 8 mWcm<sup>-2</sup>; visible light: 437 nm,  $\Delta\lambda$  23 nm, 4 mW cm<sup>-2</sup>). All photoirradiation measurements used a heat-absorbing filter to dissipate the heat generated by the mercury lamp.

## 1.6 Rheological measurement

Rheological measurements were performed on an Anton Paar MCR 301 with a hood-type temperature controller (H-PTD200) using a 25-mm diameter cylindrical rotor on a glass plate to let light through. A gap spacing of approximately 0.2 mm was used for all experiments. The elastic moduli ( $G'$  and  $G''$ ) were examined in the linear viscoelastic regime. Temperature sweep experiments were conducted with a strain amplitude of 1 % and a frequency  $\omega = 6.28$  rad/s. The intersection of  $G'$  and  $G''$  curves was taken as the critical gelation temperature of the ion gels.

## 1.7 SAXS experiments

Small-angle X-ray scattering (SAXS) experiments for the PMP solution were performed in BL-10C, Photon Factory, Japan. A monochromated X-ray beam (wavelength,  $\lambda = 1.00$  Å) was used to irradiate the samples. The solution was sealed in a plate cell with a glass cover (thickness: 30  $\mu$ m) and the thickness of the sample was 1 mm. The temperature of the sample was controlled from 25 to 80 °C

using a hot and cold stage (Instec, Inc.). The exposure time was 10 s for each measurement. The scattered X-rays were measured using a detector (PILATUS3 2M, Dectris) at sample-to-detector distances of 3.0 m. The obtained 2D data was circularly averaged and corrected for exposure time, dark current, background (cell) scattering, and transmittance.

The SAXS experiment for BMB solution was performed on the 20 wt.% sample using an Anton Parr SAXSess mc<sup>2</sup> instrument. The capillary was purchased from TOHO with a diameter of 1.5 mm. The sample was flame-sealed before conducting measurements under vacuum on a TCS120 sample holder with precise temperature control from –30 to 120 °C. It took 1 h to measure the sample after annealing for 1 h in the dark.

The obtained SAXS profiles were fitted with the Percus-Yevick hard sphere model to account for polydispersity of the core radius. In the model, the scattering intensity  $I(q)$  was described as

$$I(q) = N_s S(q) P(q)$$

where  $N_s$  is the number density of the scattering particles,  $S(q)$  is the structure factor derived from the Percus-Yevick model, and  $P(q)$  is the form factor for a sphere.  $S(q)$  can be described as

$$S(q) = \frac{1}{1 + 24\phi_{\text{HS}} G(2qR_{\text{HS}})}$$

where  $R_{\text{HS}}$  is the radius of the hard sphere and  $\phi_{\text{HS}}$  is the volume fraction of the hard sphere, which can be calculated as follows;

$$\phi_{\text{HS}} = \frac{4}{3}\pi N_{\text{HS}} R_{\text{HS}}^3$$

where  $N_{\text{HS}}$  is the number density of the hard sphere. Herein,  $G(x)$  can be defined as

$$G(x) = \frac{(1 + 2\phi_{\text{HS}})^2 \sin x - x \cos x}{(1 - \phi_{\text{HS}})^4 x^3} - 6\phi_{\text{HS}} \frac{(1 + \phi_{\text{HS}}/2)^2 2x \sin x + (2 - x^2) \cos x - 2}{(1 - \phi_{\text{HS}})^4 x^4}$$

where  $x = 2qR_{\text{HS}}$ .  $P(q)$  can be described as

$$P(q) = v^2 \Delta\rho^2 f(qR_c)^2$$

where  $v = 4\pi R_c^3/3$  is the volume of the sphere,  $\Delta\rho$  is the scattering length density difference between the sphere and solvent, and  $R_c$  is the radius of the spherical core. Herein,  $f(x)$  can be defined as

$$f(x) = \frac{3}{x^3}(\sin x - x \cos x)$$

where  $x = qR_c$ .

If a Gaussian distribution of the core radius is assumed,  $I(q)$  can be described as

$$I(q) = C_1 S(q) \left[ \int D(R_c) P(q) dR_c \right] + C_2$$

$$D(R_c) = \frac{1}{\sqrt{2\pi}\sigma_R} \exp\left[-\frac{(R_c - \langle R_c \rangle)^2}{2\sigma_R^2}\right] \text{ for } R_c \geq 0$$

where  $C_1$  and  $C_2$  are arbitrary scaling parameters,  $\langle R_c \rangle$  is the average radius of the spherical core, and

$\sigma_R$  is the standard deviation of the radius.

## 2. Figures



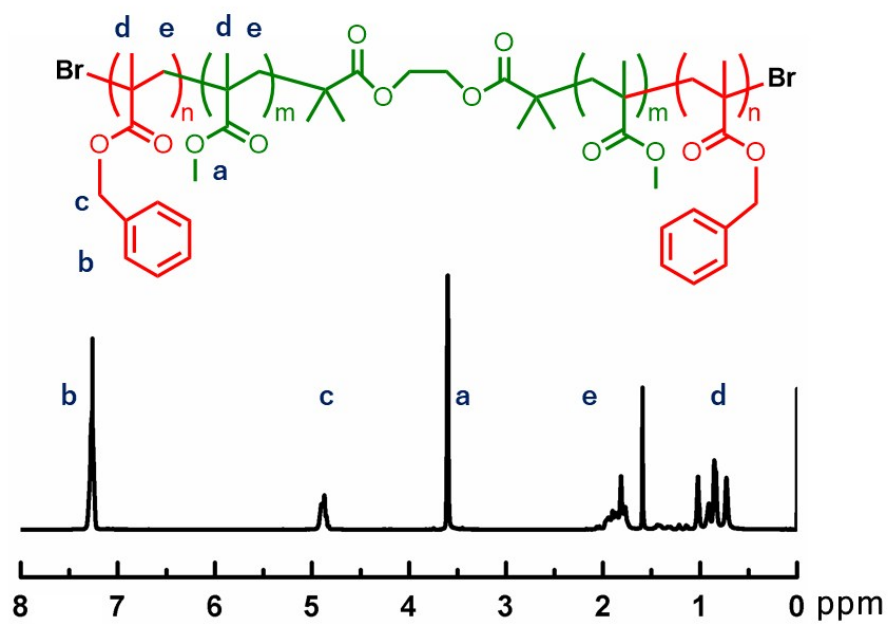
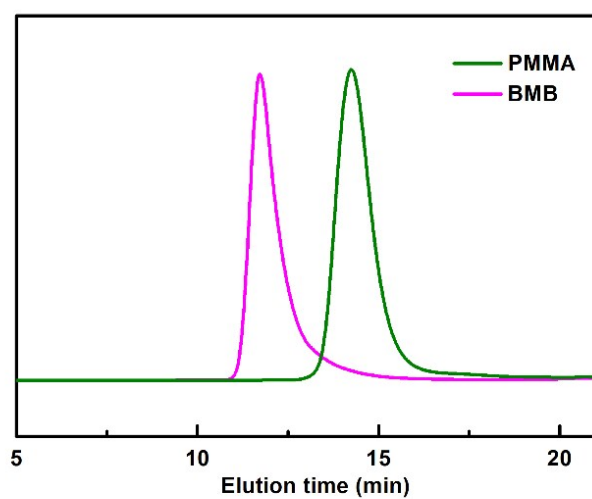
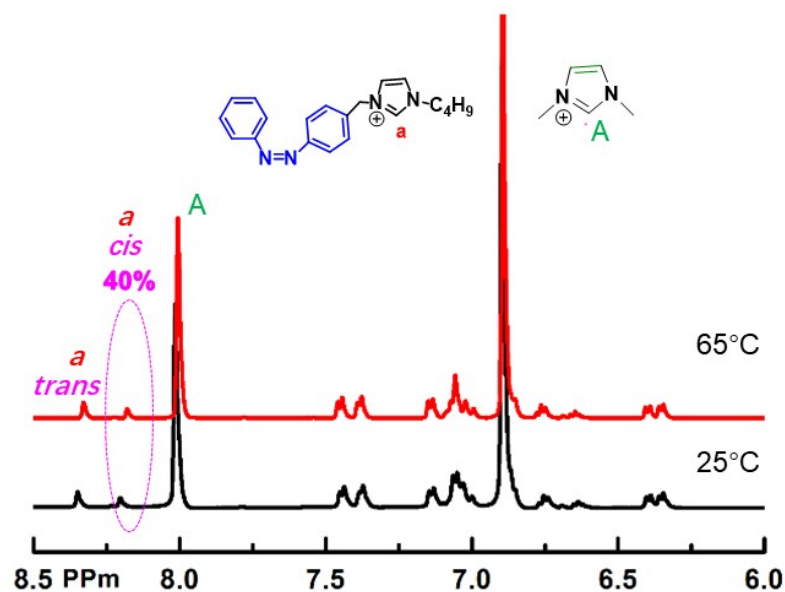


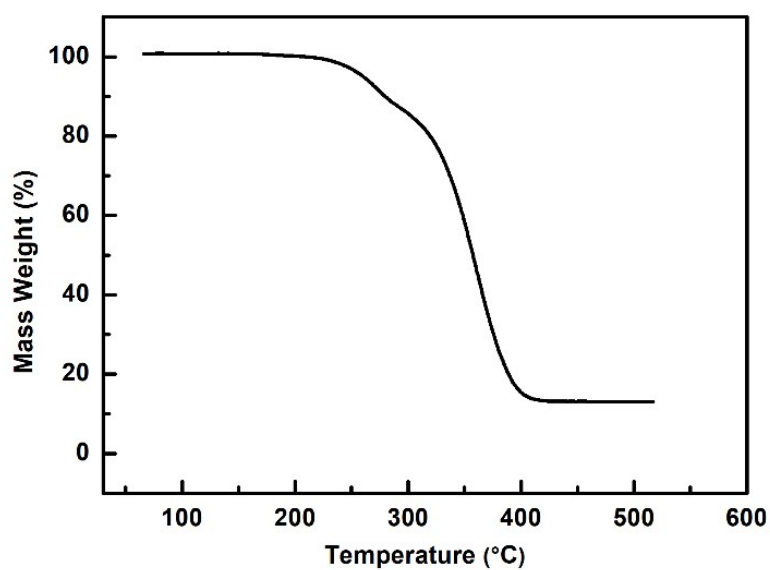
Fig. S2. <sup>1</sup>H-NMR of the BMB triblock copolymer in CDCl<sub>3</sub>.



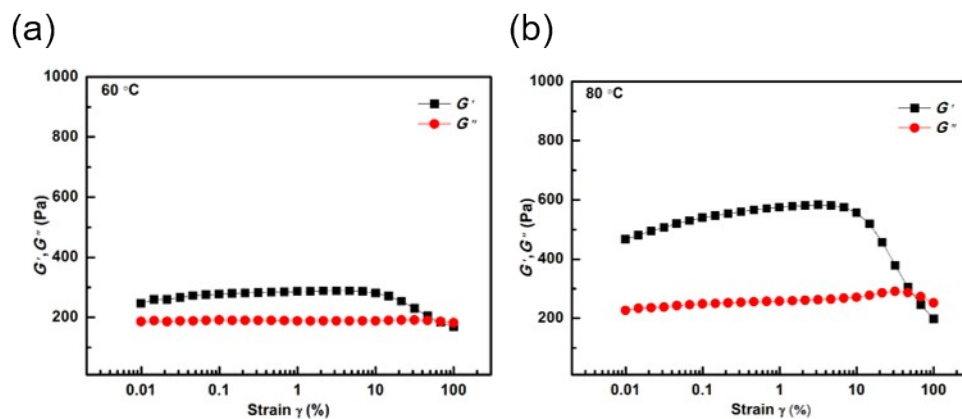




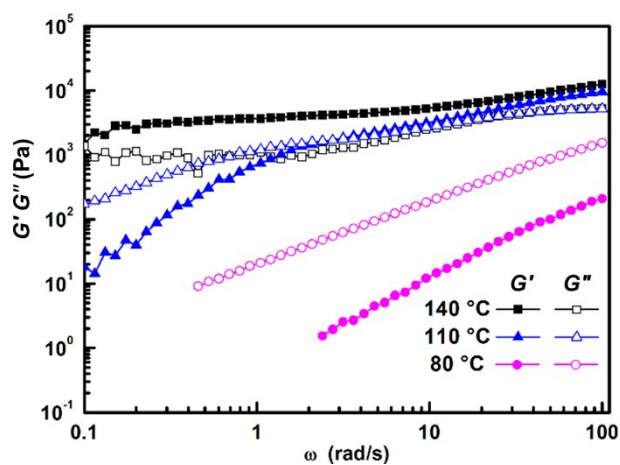
**Fig. S3**  $^1\text{H-NMR}$  spectra of mixture of  $[\text{Azo}][\text{NTf}_2]/[\text{C}_1\text{mim}][\text{NTf}_2]$  in DMSO after 30 mins UV irradiation using double-chamber NMR tube at 25 °C and 65 °C. The weight ratio of  $[\text{Azo}][\text{NTf}_2]/[\text{C}_1\text{mim}][\text{NTf}_2]$  is 5/95.



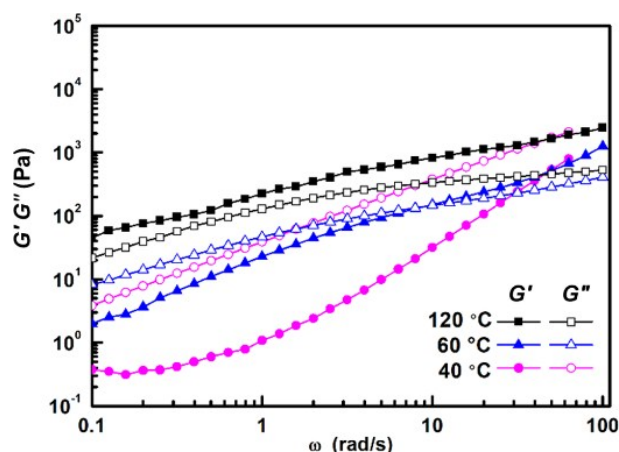
**Fig. S4** Thermal stability of the 20 wt.% BMB triblock copolymer in an IL mixture with a weight ratio of  $[\text{Azo}][\text{NTf}_2]/[\text{C}_1\text{mim}][\text{NTf}_2]$  of 5/95.



**Fig. S5** Dynamic strain sweep measurements for 20 wt% PMP solution at (a) 60 °C and (b) 80 °C.



**Fig. S6** Dynamic frequency sweep measurements for 20 wt% BMB solution at 80 °C, 110 °C, and 140 °C with a strain amplitude of 1%. The weight ratio of [Azo][NTf<sub>2</sub>]/[C<sub>1</sub>mim][NTf<sub>2</sub>] is 5/95.



**Figure S7** Dynamic frequency sweep measurements for 20 wt% PMP solution at 40 °C, 60 °C and 120 °C with a strain amplitude of 1%. The weight ratio of [Azo][NTf<sub>2</sub>]/[C<sub>1</sub>mim][NTf<sub>2</sub>] is 5/95.

## References

- 1 Y. Kitazawa, T. Ueki, S. Imaizumi, T. P. Lodge and M. Watanabe, *Chem. Lett.*, 2014, **43**, 204–206.
- 2 C. Wang, X. Ma, Y. Kitazawa, Y. Kobayashi, S. Zhang, H. Kokubo and M. Watanabe, *Macromol. Rapid Commun.*, 2016, **37**, 1960–1965.